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TRANSLATION

STUDY OF THE COMPOSITION OF THE LIGHT FRACTIONS OF SOVIET CRUDES

By A. V. Topchiyev, B. A. Kazanskiy, I. A. Musayev, G. D. Gal'pern, M. M. Kusakov, and A. F. Plate

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STUDY OF THE COMPOSITION OF THE LIGHT FRACTIONS OF SOVIET CRUDES

by

A.V.Topchiyev, B.A.Kazanskiy, I.A.Musayev, G.D.Gal'pern
M.M.Kusakov, and A.F.Plate (Moscow)

The study of the chemical composition of crudes and petroleum products is of great theoretical and practical interest. Studies establishing the relation between the composition and the physical and physicochemical properties of crudes and their cuts are of substantial importance.

Further improvement of the technology of the petrochemical industry, improvement of fuel and oil quality, increasing the assortment and yields of chemically valuable products, as well as successful solution of the problem of the extraction of petroleum, all demand continuous deepening and broadening of the information on the composition and properties of petroleum and petroleum products.

Petroleum is a highly valuable source of chemical raw materials for the production of the most diverse hydrocarbons used as intermediates for organic synthesis of substances such as alcohols, aldehydes, ketones, acids, esters, nitro products, amines, high molecular compounds (especially, synthetic rubbers and the like).

The heavy organic synthesis industry today is very closely linked with the petrochemical industry.

It must also be borne in mind that the continuous development and improvement in the design of modern engines (primarily of aircraft engines) leads to new and ever

increasing requirements on fuels and oils. At the same time the petrochemical processes, as a rule, demand rather clearly differentiated raw materials.

It has been established that various hydrocarbon and non-hydrocarbon components of petroleum fractions have widely differing fuel and lubricant properties. All this makes it necessary to develop research to improve the methods of isolating and separating the components of petroleum, and of accumulating exhaustive data on their properties. In this connection, a substantial expansion of research on the composition and properties of petroleum and petroleum fractions is necessary.

As far back as the period of formulation of the basic propositions of classical organic chemistry, whose development was based on the theory of chemical structure worked out by A.M.Butlerov, the study of the composition of petroleum attracted the attention of such great scientists as Watten, Pelouse, Kagour, Schorlemmer, Mayberry, and D.I.Mendeleyev.

Subsequent research of our countrymen was devoted to elucidating the properties of the distillates of Caucasian crudes and their comparison with Pennsylvania crudes. These studies led V.V.Markovnikov and V.N.Ogloblin to the discovery of the naphthenic hydrocarbons in Caucasian crudes and to the detailed study of the nature of these hydrocarbons.

The studies by V.V.Markovnikov, M.I.Konovalov, N.D.Zelinskiy, N.M.Kizhner, S.S.Nametkin and their numerous colleagues and pupils laid the foundations for the science of the chemistry of petroleum hydrocarbons.

At the beginning, in studying the composition of petroleum fractions, relatively simple chemical and physical methods were used: nitration, sulfonation, distillation, measurement of density, etc. For example, Mendeleyev (Bibl.1) and later Markovnikov and Ogloblin (Bibl.2), while studying the variation in density of distillates of Caucasian crudes with their boiling point, showed that the periodic character of this functional relationship was closely linked to the distribution of naphthenic and paraffinic hydrocarbons among the fractions of these crudes.

N.D.Zelinskiy synthesized several tens of individual cyclic hydrocarbons and studied their physicochemical properties, thus considerably promoting the clarification of the chemical nature of petroleum.

In 1881-1883, Beilstein and Kurbatov (Bibl.3) used the nitration method to demonstrate the presence of hexamethylene hydrocarbons in Caucasian crude, and obtained aromatic nitro derivatives. Later, in 1889-1902, appeared the classical study by Konovalov (Bibl.4) on the nitration of paraffins and naphthenes by dilute nitric acid, in which the nitration reaction was utilized to establish the structure of the hydrocarbons. These investigations culminated in the work of Nametkin (Bibl.5). During the Soviet period, the studies on the nitration of hydrocarbons were further advanced by the work of Nametkin, and by P.P.Shorygin, A.I.Titov, A.V.Topchiyev (Bibl.6), and others.

The investigation of the hydrocarbon composition of petroleum fractions by classical chemical methods (nitration, sulfonation, oxidation) involves great difficulties. The further progress of research on the composition of petroleum was directed toward the development of simpler and, at the same time, more accurate quantitative methods of determining the group and individual hydrocarbon composition of petroleum fractions. These methods combined chemical, physicochemical, and physical procedures for separating and characterizing petroleum products.

The nationalization of the petroleum industry, which radically changed its position in the USSR, permitted a decisive reorganization of the research work on petroleum.

At Baku and Grozny, at Aznefti and Groznefti respectively, central laboratories were established, and at the end of the 1920's these were reorganized into petroleum research institutes (AzNII and GrozNII).

In 1924 at Moscow, on the initiative of I.M.Gubkin, the State Petroleum Research Institute (GINI) was organized.

In 1934, the Institute of Fossil Fuels was organized in the system of the

Academy of Sciences USSR. Its organization included a number of laboratories of the GINI, and in 1948 the Petroleum Institute, AN SSSR, was organizationally separated from it.

In 1933, the Central Institute of Aviation Fuels and Oils (TsIATIM) was organized at the Central Petroleum Administration, Supreme Council of National Economy. In 1934, this institute was merged with the chemical and technical laboratories of the GINI. In 1955, it was renamed All-Union Research Institute for the Petroleum Industry (VNII NP).

The study of the composition of petroleum products by chemical and physical research methods was successfully developed in these institutes.

The work by Zelinskiy on selective catalytic dehydrogenation, which opened new paths in the study of the structure of naphthenic hydrocarbons, was of great importance for the study of the composition of petroleum fractions (Bibl.7-11).

As far back as 1911, Zelinskiy showed that cyclohexane and its homologs, when passed over such catalysts as Pt and Pd on charcoal at 300°C, are quantitatively converted into the corresponding aromatic hydrocarbons (Bibl.7). The pentamethylene hydrocarbons were not dehydrogenated, in this case.

As long ago as 1912, N.D.Zelinskiy used the reaction discovered by him to investigate the petroleum fractions of Baku crudes, and proved the presence of methylcyclohexane in them (Bibl.12).

Selective catalytic dehydrogenation subsequently became one of the most fruitful methods for investigating the structure of naphthenic hydrocarbons of petroleum. In the 1920's - 1940's, using this method, Zelinskiy, together with his colleagues and pupils of Moscow University (B.A.Kazanskiy, Yu.K.Yur'yev, N.I.Shuykin, A.M.Rubinshteyn, G.D.Gal'pern, I.A.Musayev, etc.; Bibl.13) studied the composition of the gasoline fractions of crudes from Baku, Emba, Chusov Hills, Ishimbay, and other USSR oilfields.

In the 1930's the method of catalytic dehydrogenation, based on Zelinskiy's

process, was employed at the Grozny Petroleum Research Institute to investigate the group composition of the gasoline-kerosene fractions of Grozny crudes (Bibl.14).

Kazanskiy and coworkers (Bibl.15-17) investigated the so-called "octanaphthene" and "nonanaphthene" fractions of Suraksan gasoline, and identified a number of cyclohexane homologs in it. Rubinshteyn (Bibl.18) investigated the gasoline from Fergana crude, while Yur'yev and coworkers studied gasoline from the heavy Ukhta crude, Changartysh crude, and a number of Central Asian crudes (the Shorsu, Khaudag oilfields, etc.) (Bibl.19-23).

Zelinskiy and Kazanskiy (Bibl.24) first demonstrated the presence of decalin in Baku gasoline and showed the applicability of the method of catalytic dehydrogenation to the investigation of the composition of petroleum fractions boiling higher than the gasoline.

Yur'yev and Musayev studied the group chemical composition of the gasoline-kerosene fraction of Kalin crude (Bibl.25).

Zelinskiy, Musayev, and Gal'pern, using catalytic dehydrogenation, investigated the group chemical composition of a series of five-degree gasoline-ligroin cuts, taken from the Jurassic crude of the Kos-Chagyl fields in the range from 30 to 250°C (Bibl.26, 72). An exceptionally high content of cyclic hydrocarbons (~ 80%) was found in these fractions. In the gasoline fractions up to 215°C, hexahydroaromatic hydrocarbons predominate among the cyclic compounds.

In 1935, Panyutin and Firsanova (Bibl.28), using rectification and catalytic dehydrogenation, studied the chemical composition of Surakhan gasoline. The authors succeeded in estimating the concentration of the individual hexa- and pentamethylene hydrocarbons and in showing that the gasoline consisted primarily of methylcyclohexane, cyclohexane, and 1,4-dimethylcyclohexane. The presence of p-xylene, which could be separated in the pure form, was detected in the catalyzate.

The group composition of the gasoline-ligroin fractions of 18 individual Soviet crudes was studied by Gal'pern (Bibl.29-31).

All the above-listed studies showed the content of cyclopentanes and cyclohexanes to vary widely in the gasolines produced from the crudes of various deposits in the USSR.

A group of scientific workers at the Grozny Petroleum Research Institute (M.D.Tilicheyev, R.D.Virabyants, L.G.Zherdeva, A.N.Doladugin, M.G.Yegorova at el, under the supervision of A.N.Sakhanov), in the early 1930's, developed the analysis methods for the group composition of petroleum fractions. The method of "aniline point" found very wide use (Bibl.14). The method of determining the group chemical composition of crudes and petroleum products proposed by GrozNII is still being used at research and plant laboratories.

The basic trend of the research by the GINI and IGI was, at first, the refinement and further differentiation of the method of group analysis of straight-run petroleum products.

A considerably more complex problem arises in the analysis of the group chemical composition of cracked gasolines, which in some cases contain over 30% of unsaturated compounds.

The first difficulty encountered by the investigator studying the group composition of cracked gasolines is that most of the reagents ordinarily used to determine the content of unsaturated hydrocarbons also affect the aromatic hydrocarbons more or less, and lead to a partial polymerization of the unsaturated hydrocarbons. Tilicheyev and Masina (Bibl.14), at the GrozNII, proposed a standard method based on the use of "aniline factors", to determine the content of unsaturated and aromatic hydrocarbons in standard wide cuts. In another version of the technique, the percentage of unsaturated hydrocarbons is calculated from the iodine number and the molecular weight of the fraction. The two versions of the methods include the total removal of the aromatic and unsaturated hydrocarbons by sulfonation.

Nametkin and Robinzon (Bibl.32-34) have proposed an improved method of step analysis of the group chemical composition of cracked gasolines. It consists in first

determining the total olefins (by means of sulfur monochloride), and then of the aromatic and naphthenic hydrocarbons (by the aniline method).

Gal'pern and Vinogradova (Bibl.35-38) gave a critical analysis of the Max-Illiney bromometric method, and first applied the Kaufman bromometric method to the analysis of petroleum products. This method was subsequently carefully developed and found wide use in laboratory practice. These methods determine only the total unsaturated hydrocarbons, but do not determine the types of unsaturated compounds present.

Zelinskiy and Levina (Bibl.39, 40) have catalytic applied hydrogenation-dehydrogenation, in conjunction with the sulfuric acid method, to establish the relative concentration of cyclic and aliphatic unsaturated hydrocarbons in cracked gasolines.

Terent'yev, Gal'pern, and Vinogradova (Bibl.41) have proposed a diazometric method of determining the conjugated dienes in cracked gasolines, in conjunction with bromometry, to differentiate the unsaturated hydrocarbons in secondary gasolines.

An indirect indication of the structure of unsaturated hydrocarbons is given by the amount of hydrogen bromide liberated on running a bromometric determination, as stated by Gal'pern (Bibl.38) and also by A.A.Petrov (Bibl.42). Petrov establishes the possibility of explaining this phenomenon on the basis of Tishchenko's views on the halogenation of unsaturated hydrocarbons, which he developed in the 1940's (Bibl.43).

Musayev and Gal'pern, from a number of individual unsaturated and aromatic hydrocarbons and their mixtures, have shown that copperized asbestos, under certain conditions, under hydrogen pressure, will selectively hydrogenate only the unsaturated hydrocarbons (Bibl.44-46).

On the basis of this work in the Petroleum-Chemistry Laboratory imeni S.S.Nametkin, the researchers Topchiyev, Musayev, and Gal'pern have proposed a combined method of investigating the detailed group chemical composition of cracked

gasolines (Bibl.47). This method includes the total removal of unsaturated and aromatic compounds by sulfuric acid, selective hydrogenation of the unsaturated hydrocarbons, and analytical dehydrogenation of the hexahydroaromatic hydrocarbons. The method permits determination, in standard cuts of cracked gasoline (free of sulfur compounds), of the following groups of hydrocarbons: aromatics, alkenyl-aromatic alkenes, alkanes, cyclenes, and cyclanes (the six- and five-membered compounds separately).

With the proposed method, the authors investigated thermally cracked and catalytically cracked gasolines produced from Grozny paraffinic crude. They found that the 60 - 200°C cut of the thermally cracked gasoline was characterized by a high content of unsaturated hydrocarbons, mainly alicyclic, and by the presence of an appreciable concentration of unsaturated hydrocarbons with a six-member ring. The 60 - - 200°C cut of catalytic-cracked gasoline shows a low content of unsaturated hydrocarbon, consisting in almost equal amounts of aliphatic compounds and compounds with a five-member ring, at almost complete absence of six-membered unsaturated hydrocarbons.

By means of the same method, Glushnev and Nepryakhina (Bibl.48, 49) investigated the composition of gasolines from oxidative cracking and from reforming.

Mamedaliyev and Rzayeva have shown the possibility of selective hydrogenation of the unsaturated hydrocarbons in various fractions of thermally cracked gasoline and of pyrolysis over a kieselguhr-supported nickel catalyst at various temperatures in a stream of hydrogen (Bibl.50).

In investigating the group composition of the gasoline fractions of petroleum, since the 1940's, workers have used the refractometric and dispersion methods, based on the assumption of additivity of the specific refraction and dispersion of the components of hydrocarbon mixtures (Bibl.51-54). In particular, methods of determining the aromatic hydrocarbons in gasolines, based on this principle, are widely used.

Tilicheyev and Okinshevich (Bibl.55, 56) have developed a cryoscopic method of

quantitative determination of aromatic hydrocarbons, and of the total quantity of aromatic and unsaturated hydrocarbons in gasolines, kerosenes, and diesel fuels, using cyclohexane as the solvent.

The rapid growth of petroleum extraction in the deposits of the Second Baku have confronted our research organizations with the problem of finding more rational methods of refining sulfur-bearing crudes. In this connection, studies of sulfur compounds in crudes and petroleum products have become particularly important, as has the development of desulfurization methods for crudes. The results of research in this field should be discussed separately.

Nametkin paid great attention to the possibility of analytical use of the reaction of nitration of aliphatic and paraffinic hydrocarbons. Thus Nametkin, Nifontova, and Amirkhanova (Bibl.57, 58), by the nitration of brown-coal paraffin, petroleum paraffin and petroleum ceresin, obtained interesting conclusions on the chemical structure of the hydrocarbons composing the paraffins and ceresins.

A comparative study of the composition and properties of gasolines, kerosenes, and lubricating oil produced from Soviet crudes has been initiated at the Petroleum-Chemistry Laboratory of the GINI, and later at the Institute of Fossil Fuels, Academy of Sciences USSR, under the supervision of S.S.Nametkin.

In collaboration with Putsillo, Nifontova, Shakhnazarova and Abakumovskaya, Nametkin (Bibl.59) has given a general chemical characterization of a number of Sakhalin crudes (Okha, Nutovo, Katangli, Ekhabi, Chakry, Lyangri deposits), of Kamchatka crude (Bogachevsk deposit), and of Ural crude (Perm deposit), etc.

The group chemical composition of the bright fractions of a number of Caucasian crudes had already been investigated in detail in the 1920's - 1930's by the members of the GrozNII already mentioned (Bibl.14).

A group of workers at the Azerbaydzhan Petroleum Research Institute imeni V.V.Kuybyshev (AzNII), under the supervision of A.M.Plotko, has systematically investigated the crudes of Azerbaydzhan, Georgia, and Trans-Caspia, which were later

studied by V.S.Gutyri as well. The results of these studies have been collected in a monograph authored by Gutyri, Masumyan, Bukh, and Lisovskaya (Bibl.60).

S.N.Pavlova, A.S.Velikovskiy, E.V.Driatskaya, L.A.Potolovskiy and others at the Petroleum Industry Research Institute have developed a single method for the typical analysis of USSR crudes and on the basis of the materials obtained, have given data for their assay certificates.

The results of many years of work under the supervision of Velikovskiy and Pavlova, first at the GINI and then at the VNII NP, have been collected in a manual (Bibl.61) and in a monograph (Bibl.62).

Under the direction of Ye.A.Robinzon, at the Chemical Institute imeni A.Ye.Arbuzov, Kazan Branch Academy of Sciences USSR, at the Petroleum-Chemistry Laboratory, a systematic study has been going on since 1946 of the Tatar crudes, which are of great industrial importance. These studies have been collected in a monograph (Bibl.63) giving the physical properties and the results of group and ring chemical analysis of the hydrocarbons of these crudes. In 1957, these data were substantially supplemented (Bibl.64).

All the above materials refer to the characterization of the group chemical composition of petroleum distillates and play an important part in evaluating the quality of crudes and petroleum products from their group criteria, especially with respect to the low-boiling, gasoline and kerosene fractions.

Together with studies of the group chemical composition of crudes and petroleum products, performed for the most part at the laboratories of the petroleum industry, at the Academy of Sciences USSR (Petroleum Institute and Institute of Organic Chemistry), and at Moscow University, work has also been done on the individual composition of straight-run gasoline (N.D.Zelinskiy, B.A.Kazanskiy, G.S.Landsberg, and A.V.Topchiyev).

The first attempts to use the Raman-spectrum method for the analysis of light petroleum products were made in the USSR in 1938 at the Institute of Physical Chemis-

try imeni Karpov by Vol'kenshteyn and Shorygin, who investigated the individual composition of a number of fractions of several natural gasolines, cracked gasolines (without unsaturated hydrocarbons), and synthene (Bibl.65-68).

Kazanskiy and Gasan-Zade (Bibl.69) have studied the composition of the fractions of Kala crude, in one of the first examples of the successful combination of the method of catalytic dehydrogenation with the Raman-spectrum method, applied to a mixture of cyclopentane hydrocarbons and paraffinic hydrocarbons.

These studies began to achieve particular success after the development of a Raman-spectrum method of quantitative analysis of the individual composition of straight-run gasoline fractions with an end point of 150°C (Bibl.70), under the supervision of B.A.Kazanskiy and G.S.Landsberg, by a group of workers at the Institute of Organic Chemistry imeni N.D.Zelinskiy, Academy of Sciences USSR (A.F.Plate, Ye.A.Mikhaylova, A.L.Liberman, et al) and the Physical Institute imeni P.N.Lebedev, Academy of Sciences USSR (P.A.Bazhylin, M.M.Suskiy, et al).

This method is based on the chromatographic separation of aromatic hydrocarbons from the naphthenic and paraffinic hydrocarbons, followed by an analytical dehydrogenation of the dearomatized portion, and repeated chromatography of the catalyzate.

The initial aromatic hydrocarbons, as well as the aromatic hydrocarbons newly formed as a result of the analytical dehydrogenation, and the residue of undehydrogenated paraffins and naphthenes (pentamethylene and unsubstituted hexamethylene hydrocarbons) are separately distilled into narrow cuts in an efficient column. The composition of the resultant narrow cuts is investigated by means of the Raman-spectrum. The successful application of the Raman-spectrum method necessitates a careful and systematic study of the Raman spectra of the individual hydrocarbons that might be present in the fractions under investigation.

A large number of high-purity individual hydrocarbons of various classes have been prepared at the Institute of Organic Chemistry Academy of Sciences USSR by B.A.Kazanskiy and associates. The Raman spectra of these hydrocarbons have been

studied at the Physical Institute imeni P.N.Lebedev, Academy of Sciences USSR.

The Raman spectra of several hundred individual hydrocarbons, carefully measured, have now been obtained by P.A.Bazhulin, Kh.Ye.Stern et al (Physical Institute imeni P.N.Lebedev, Academy of Sciences USSR and Spectroscopic Commission, Department of Physical and Mathematical Sciences Academy of Sciences USSR), by V.M.Tatevskiy and associates (Moscow State University), and by a number of other Soviet investigators. Sushchinskiy (Bibl.71) has solved the question of rationally measuring the intensity of the spectral lines, and has worked out a method of conversion of the intensities of lines measured in different systems. An atlas has been compiled as a result of this work (Bibl.73). It contains the Raman spectra of 278 hydrocarbons, with the line intensities reduced to a single system, permitting a reliable quantitative analysis.

Based on this Raman-spectrum method, and to provide grounds and verification for it, a systematic study of the individual composition of straight-run gasolines from various USSR crudes was commenced in 1948 at various laboratories.

This work was performed at the Institute of Organic Chemistry imeni N.D.Zelinskiy under the direction of B.A.Kazanskiy by A.F.Plate, Ye.A.Mikhaylova, A.L.Liberman et all in collaboration with the Physical Institute imeni P.N.Lebedev Academy of Sciences USSR, under the direction of G.S.Landsberg, by P.A.Bazhulin, M.M.Sushchinskiy and others (Bibl.74-80); and at the Petroleum Institute, Academy of Sciences USSR, under the direction of A.V.Topchiyev, by I.A.Musayev, G.D.Gal'pern and A.I.Kislinskiy (Bibl.81-91).

A total of 11 gasolines from crudes of various deposits were investigated. These deposits were as follows: Azerbaydzhan (three samples of Surakhan, two samples of Kazanbulak and Karachukhur), Turkmenia (Nebit-Dag of the central region, red strata and western region, Akchagyl' stage), Kazakhstan (Emba, Koschagyl), Bashkir (Tuymazy), and Tatar (Romashkin, Mininbayev structure).

The method used at the petroleum institutes for examining gasolines from the

Surakhan ordinary crude and from the crude of the Central Nebit-Dag, differs somewhat from the Raman-spectrum method (Bibl. 83, 84, 85). Here the naphthene-paraffin portion of the gasolines, prior to the hydrogenation but after chromatographic separation of the aromatic hydrocarbons by silica gel, was distilled in a column equivalent to 100 theoretical plates into narrow cuts boiling from 60 to 150°C (about 40 fractions), after which the Raman spectra of these fractions were recorded and examined. The fractions were then dehydrogenated, and the Raman spectra of the resultant catalyzates were recorded. The subsequent operations were dearomatization of the catalyzates, and spectral analysis of the pentamethylene-paraffin residue. This analytical procedure permitted an elucidation of the degree of the side processes (cyclization, hydrogenolysis, etc.) accompanying the analytical dehydrogenation; in this way, the ratio of the individual stereoisomeric forms of the disubstituted and polysubstituted cyclohexane and cyclopentane hydrocarbons in the gasoline fraction could be estimated.

The gasoline of the Nebit-Dag crude (from the central region) which had not been subjected to catalytic dehydrogenation showed several stereoisomeric forms of cyclohexane and cyclopentane hydrocarbons.

The predominance of the cis-1,3-disubstituted hydrocarbons over the trans-forms was shown, as well as the predominance of the trans-1,2 and the trans-1,4-disubstituted hydrocarbons over the corresponding cis-forms. In other words, the thermodynamically more stable forms were predominant.

In this work, it was experimentally demonstrated that the fundamental reaction during an analytical dehydrogenation was a conversion of the hexahydroaromatic hydrocarbons into the corresponding aromatics. Neither cyclization nor aromatization of the paraffinic hydrocarbons was observed. The hydrogenolysis of the pentamethylene ring, under the conditions adopted for analytical dehydrogenation, was not entirely excluded. Its role, however, was apparently insignificant. In the corresponding gasoline fraction, the 1,1-dimethylcyclohexane is partially converted into

toluene, with a simultaneous liberation of methane (Kazanskiy and Liberman reaction). The interconversion of the cis- and trans-forms of certain cyclopentane hydrocarbons is possible (Bibl.85, 89, 90, 91).

By comparing the spectra of the 136 - 150°C fractions before and after dehydrogenation, the probable frequency of several analytical lines was established for the spectra of certain hexamethylene hydrocarbons for which the literature has either no data at all, or gives data only for the spectra of mixtures of stereoisomers.

Topchiyev, Musayev, and Gal'pern have recently shown that, on dehydrogenation of the naphthene-paraffin portion of gasoline, certain amounts of unsaturated compounds are formed. It was chromatographically possible to separate from the catalyzate a mixture of unsaturated hydrocarbons with a boiling range of 78 - 140°C and with a mean iodine number of 290. It was established from the Raman spectra (by I.A.Kislinskiy) that the unsaturated hydrocarbons consist of olefins and cyclo-olefins.

An investigation of the individual composition of straight-run gasolines showed then to contain as many as 120 - 130 hydrocarbons. This is no less than 70% of the total number of possible hydrocarbons in the same boiling range. With such an abundance in the general composition of the gasoline, the concentration of the individual hydrocarbons is extremely varied. Thus the five most abundant hydrocarbons in each gasoline made up from 18 to 36% of the entire sample. Other USSR gasolines exhibit the same characteristic feature in their composition (Bibl.74-78).

Similarity of the chemical composition and physical properties of the hydrocarbons was established for the gasolines from the Nebit-Dag crudes and the Kazanbulak and Karachukhur crudes as well as for the gasolines produced from the Devonian crudes of the Romashkin and Tuymazy oilfields.

The most characteristic features of the composition of the straight-run gasolines examined were as follows: The hydrocarbon composition of the gasolines from the Central Nebit-Dag crude (from the red stratum) differs strongly from that of the

gasolines from the Western Nebit-dag crude (from the Akchagyl' stage). The former is higher in naphthenes and isoparaffins. In chemical composition and physical properties, the gasolines from the Nebit-dag crudes approach those from the crudes of the Azerbaydzhan oilfields (Karachukhur and Kazanbulak). The gasoline from the Devonian crudes of the Mininbay structure of the Romashkin oilfield in Tatary has a hydrocarbon composition and physical properties resembling those of the gasoline from the Devonian crudes of the Tuymazy oilfield in Bashkiria, and is distinguished by its elevated content of normal paraffins. The Romashkin gasoline differs from the Tuymazy product in its elevated content of 2-methylpentane and 2-methylhexane. The gasoline from the Jurassic Koschagyl crude is high in cyclohexane hydrocarbons and resembles the composition of the gasoline from Surakhan selected crude and from Nebit-dag crude from younger strata. The gasoline from the Surakhan oily crude differs sharply from the gasolines from the Surakhan ordinary crude in that it has a higher content of normal paraffins. The same difference is observed for the two Kazanbulak crudes. In both cases, the difference in the gasoline composition is apparently connected with the difference in the depth of the oil deposits. The gasolines from Karachukhur crude are distinguished by high contents of toluene, n-paraffins, and ethylcyclohexane. The First Kazanbulak crude is characterized by gasoline with elevated isoparaffins.

Kazanskiy, Landsberg and Plate, with their associates (Bibl.72, 80), have applied the Raman-spectrum method of examining gasolines to the aromatic and hexahydroaromatic hydrocarbons of the ligroin from the Emba crude of the Koschagyl field.

Shuykin, Novikov, and Naryshkina (Bibl.92), using the Raman-spectrum method and oxidation with a potassium permanganate solution, investigated the content of individual aromatic and hexamethylene hydrocarbons in the 136 - 144°C, 144 - 150°C, and 150 - 156°C fractions of Maykop gasoline. They found these fractions to contain mono-, di-, and tri-substituted homologs of cyclohexane and benzene.

Zizin, Yasnopol'skiy, and Ashumov, at the Azerbaydzhan Petroleum Industry Re-

search Institute imeni Kuybyshev (Bibl.93), invertigated the gasolines from 15 Baku crudes by a simplified Raman-spectrum method (Surakhan selective, Surakhan ordinary, Upper Kalinin, Lower Kalinin, Kalinin suite, Upper Permian, Lower Permian, Gyurgyav, Balakhan oily, Binagad, Upper Karachukhur, Lower Karachukhur, Umbak, Neftyanyye Kamni, Bibi Eybat waxy). They found that all the gasolines examined, (except the gasolines from the Gyurgyav crude) contained more naphthenes than paraffins. Among the naphthenes, the cyclohexane hydrocarbons predominated over the cyclopentanes; among the paraffins, the isohydrocarbons predominated. In all these gasolines, the content of aromatics was exceedingly low, except for the gasoline from the Lower Karachukhur crude, which did contain 5.8% of toluene. The crudes with high cyclohexane and methylcyclohexane were of the greatest interest.

The cyclohexane content of the gasolines from some crudes ran as high as 8.5%, and the methylcyclohexane as high as 23.6%.

Pishnamazzade and coworkers, at the Petroleum Institute, Academy of Sciences AZSSR (Bibl.94, 95), used the Raman-spectrum method to investigate the individual hydrocarbon composition of straight-run gasolines from the marine deposits of the PK and KS suites of the Neftyanyye Kamni. They found the naphthenes to predominate in the gasoline from the PK suite, and the paraffins in that from the KS suite. Among the paraffins in the gasoline from the PK and KS suites, paraffins with one and two tertiary carbon atoms predominate. The gasoline from the PK suite contains more cyclohexanes, cyclopentanes, and normal paraffins than the gasoline from the KS suite.

These authors detected methylcyclopentane by the Raman-spectrum method, in the 127 - 133°C and 133 - 138°C fractions of the KS suite and in the 127.5 - 132°C and 132 - 136°C fractions of the gasoline from the PK suite. This observation requires further physicochemical justification.

Khodzhayev, at the Institute of Chemistry, Academy of Sciences Uzbek SSR, studied the individual hydrocarbon composition of Fergana gasolines by the Raman-

spectrum method, and also worked out a chemical method of analysis of mixtures of mono-, di-, tri-, and tetra-substituted aromatic hydrocarbons, and the aromatic hydrocarbons formed on dehydrogenation of hexamethylene hydrocarbons, by oxidizing them to the corresponding aromatic acids. This method is based on the differential solubility of the acids themselves, and of their derivatives, in different solvents. By using this technique for separating a mixture of aromatic acids, he quantitatively determined 14 aromatic hydrocarbons in the 56 - 175°C cut (Bibl.96).

He also studied the content of individual aromatic and cyclohexane hydrocarbons (after dehydrogenation) in two samples of gasoline from the crudes of the Southern Alamyshik and Andizhan deposits. He found that tri-substituted aromatic hydrocarbons, with short side chains, predominated in the 150 - 175°C cut, and also found mono- and di-substituted hydrocarbons with long side chains in insignificant amounts.

Agafonov, Nikolayeva, Zimina and Abayev, at the All-Union Petroleum Industry Research Institute (Bibl.97), studied the individual hydrocarbon composition of fractions from paraffin-base crudes (Romashkin and Tuymazy), gasolines from naphthene-base crudes (Ekhab, Baku, and gasoline from Zhirnov crude), of catalytic-cracked gasoline and high-octane components, alkylates, and technical iso-octane. He obtained very interesting results on the gasoline fractions of the Zhirnov crude, with a high octane number containing only 3% of aromatic hydrocarbons, and free from cyclopentane, methylcyclopentane, cyclohexane, and methylcyclohexane. The high content of isoparaffins and the complete absence of normal paraffins is characteristic for this gasoline.

Urmancheyev and Robinzon and associates (Bibl.98) used the Raman-spectrum method to investigate the individual hydrocarbon composition of two samples of straight-run gasoline with an end point of 150°C, from crudes of the Bavly and Romashkin fields of Tatary.

They proved that the chemical composition of the gasolines studied, from the crudes of the same age and from one and the same horizon, were the same.

Niyazov and coworkers, at the Institute of Chemistry, Academy of Sciences Turkmenian SSR, is systematically studying the group and structural-group composition of fractions of crudes from the Nebit-dag, Kum-dag, and Cheleken fields (Bibl.99-101).

Amosov (Bibl.102) applied the Raman-spectrum method to a study of the composition of gasolines from two Turkmenian crudes, to elucidate the relation between the compositions of the light and heavy portions of each crude and the conditions of thermodynamic equilibrium between the individual gasoline components.

Areshidze, at the Institute of Chemistry, Academy of Sciences Georgian SSR, has systematically studied the group composition and types of hydrocarbons of the gasoline-ligroin fractions of the crudes of the Georgian oilfields (Mirza and Supsa) using the method of catalytic dehydrogenation (Bibl.103-106).

Razumov and Podkletnov, at the Institute of Chemistry, Sakhalin Branch, Academy of Sciences USSR, have recently been studying the individual composition of the aromatic, hexamethylene, and condensed aromatic hydrocarbons of the gasoline-kerosene fractions of Sakhalin crudes (Bibl.107).

Studies of the individual composition of a large number of the gasoline fractions of USSR crudes disclose the presence of over 100 hydrocarbons, which constitutes about 80% of the total number of all possible saturated and aromatic hydrocarbons in the boiling range of these fractions. The Raman-spectrum method, which is widely used in petroleum laboratory practice, may thus be considered a useful tool in solving the problems connected with the study of the individual composition of straight-run gasoline fractions.

The discovered irregularities in the concentration distribution of individual hydrocarbons and the existence of specific differences between the composition of crudes even from a single oilfield make it particularly important to accumulate systematic data on the content of individual hydrocarbons in USSR crudes. Unfortunately, it seems that during the last few years investigations of the exact composition of

straight-run gasolines have not reached the level specified by the resolutions of the All-Union conference on the study of the composition and properties of crudes and petroleum products, held at Moscow in January 1956.

The detailed analysis of cracked gasolines which contain unsaturated hydrocarbons is considerably more complicated than the analysis of straight-run gasolines. Several attempts have been made to utilize Raman spectra for studying the individual composition of cracked gasolines.

At the Petroleum Institute Academy of Sciences USSR, in the petroleum chemistry laboratory (with the participation of the Laboratory of Petroleum Physics and Physical Chemistry) a Raman-spectrum method is being developed since 1955, under the direction of A.V.Topchiyev, I.A.Musayev, E.G.Iskhakova, A.N.Kislinskiy, and G.D.Gal'pern, for investigating the individual hydrocarbon concentration of cracked gasolines, using separation by chromatographic absorption, analytical catalytic hydrogenation and dehydrogenation, and Raman-spectrum analysis.

One of the objects of study was the refinery pressure distillate of thermally cracked gasoline, produced from the residuum of Grozny waxy crude. Two fractions, boiling up to 60°C and in the range of 60 - 150°C, were separated from the gasoline in a microfractionator.

Investigations of the individual hydrocarbon composition of the narrow cuts boiling up to 60°C were conducted by the Raman-spectrum method. It was found that, in both the straight-run and cracked gasolines, there was a marked predominance of some hydrocarbons over others. Thus, the three hydrocarbons n-pentane, 2-methylbutane and 2-methyl-2-butene, taken together, composed about 50% of the total amount of the fractions up to 60°C (Bibl.108).

The conditions of a chromatographic method for separating the unsaturated hydrocarbons into hydrocarbon classes was worked out on natural and artificial mixtures.

By means of the proposed method, the 60 - 150°C cut of a cracked gasoline was

separated into naphthene-paraffin, unsaturated, and aromatic classes of hydrocarbons (Bibl.109).

The individual composition of aromatic and hexamethylene hydrocarbons (after dehydrogenation of the naphthene-paraffin portion, followed by separation of the freed aromatic hydrocarbons on silica gel) was studied by the Raman-spectrum method.

Toluene and m-xylene predominated in the aromatic portion and, together, composed 53%. In the hexamethylene portion, methylcyclohexane and ethylcyclohexane together made up 46% (Bibl.110).

The composition of the olefins and cycloolefins was studied from the spectra of the narrow original fractions before and after hydrogenation, and also by the aniline method. To define the degree and order of the substitutions at the double bond of the olefin molecules, narrow olefin cuts were subjected to group analysis from the characteristic Raman frequencies. In the fractions boiling above 100°C, the hydrogenation products were dehydrogenated to establish their content of hexamethylene compounds (Bibl.111).

The composition of narrow cuts of the pentamethylene-paraffin portion was studied by the Raman-spectrum method.

Other investigators have also attempted a partial analysis of the composition of cracked gasolines by the Raman-spectrum method. Thus, Mamedaliyev and associates (Bibl.112) used this method, parallel with the chemical method, to investigate the pentane-pentene fraction of a cracked gasoline. Tilicheyev and associates (Bibl.113) (TsIATIM and Moscow State University) applied this method, with a methodological object, to a quantitative analysis of the composition of aromatic hydrocarbons in fractions of cracked gasolines, to which these hydrocarbons had artificially been added.

Recently, in connection with the vigorous growth of jet aviation and diesel engine use, the medium-boiling ligroin-kerosene fractions of crude have become particularly important.

The investigation of the chemical composition of the straight-run ligroin-

kerosene fractions of crude involves great difficulties, since their composition is more complex than that of the gasolines. In this connection, the task of studying the composition of the kerosene fractions of crudes does not consist in characterizing the individual hydrocarbon composition (which is possible for the straight-run gasoline fractions) but only in a more or less detailed characterization of the hydrocarbon types and groups: of the aromatic, naphthene, and paraffin series.

Research originally started both in the USSR and abroad toward working out a group analysis method for the composition of relatively wide kerosene fractions of crude. The study of high-boiling fractions by the classical methods of organic chemistry showed that the unusual complexity of their composition would make it necessary to use a group of more modern physicochemical and physical methods of analysis. V.V.Markovnikov already understood the inadequacy of the classical methods and turned to I.I.Kanonnikov to confirm his conclusions on the cyclic nature of the naphthenes by physicochemical methods. At the chemical laboratory of Kazan University, Kanonnikov (Bibl.114) first demonstrated the ring structure of the naphthenes studied by Markovnikov and of certain terpenes investigated by Wagner, using the refractometric method. This method, in conjunction with others, was the basis of the so-called "ring analysis" proposed by Fluegter and Waterman. This method was later considerably improved by the authors themselves and by other investigators.

Under the direction of N.D.Zelinskiy, Gal'pern and Musayev (Bibl.115-118) applied the refractometric method to the analysis of narrow cuts of saturated hydrocarbons from the kerosene, oil and higher boiling fractions of Koschagyl crude. These authors worked out a version of the apparatus setup for analytical pressure hydrogenation and showed that aromatic hydrocarbons of various structure could be hydrogenated without changing their structure.

The picrate method has been widely used in recent years to investigate the condensed aromatic hydrocarbons in the kerosene fractions of petroleum.

Nametkin and Pokrovskaya successfully applied the picrate method to the qualita-

tive analysis and, in isolated instances, to the semiquantitative analysis of the naphthalene homologs in the kerosene fractions of a number of USSR crudes.

Systematic studies of the kerosene fractions of crudes from various regions of the USSR showed the presence of naphthalene, methylnaphthalenes, di- and trimethylnaphthalenes, and tetramethylnaphthalenes. Romashkin kerosene is an exception. Here a mixture of isomers of dimethylisopropylnaphthalene was noted.

In investigating the kerosene fractions of Emba crudes it was found that the kerosene produced from Makat crude did not contain naphthalene or its homologs, while the kerosenes from Dossor crude contains condensed aromatic hydrocarbon (Bibl.119, 124).

Robinzon and Grishina investigated the kerosene fractions of Bavly crude by the picrate method (Bibl.125).

Applying catalytic dehydrogenation to the kerosene fractions separated after removal of the aromatics over silica gel, Rozenberg and Nifontova (Bibl.126, 127) ascertained the content of decalin-series hydrocarbons in the kerosenes produced from Surakhan and Dossor crudes, and established their structure. They showed, at the same time, that decalin and its homologs are present together with the corresponding homologs of naphthalene.

Rozenberg, in connection with the study of the composition of the kerosene fractions of petroleum, refined a technique of separating the normal paraffins from their mixtures with isoparaffins and naphthenes by the carbamide method (Bibl.128, 129). Topchiyev, Rozenberg, Nechitaylo, and Terent'yeva studied the properties of crystalline complexes of n-paraffins with carbonate and investigated systems of individual paraffins by the thermographic method (Bibl.130-134).

The compilation of absorption spectra of individual hydrocarbons is of great importance for the examination of petroleum fractions by ultraviolet absorption spectroscopy (as it is also the case for other spectral methods).

Entirely insufficient attention has been paid up to now to the synthesis of

high-purity individual hydrocarbons, and to their spectral examination by means of USSR instruments. Only two papers have been published giving the results of a study of ultraviolet absorption spectra of individual aromatic hydrocarbons (in solution). On analysis of gasolines by the photographic method, Shtandel' and Shostenko (Bibl.135) found the near-ultraviolet absorption spectra of benzene, toluene, o-, m-, and p-xylenes, ethylbenzene, psuedocumene, m-diethylbenzene and propylbenzene. Thus, in investigating the individual composition of gasolines by ultraviolet absorption spectrophotometry, Zimina and Siryuk (Bibl.136, 137) obtained the absorption spectra of benzene, toluene, o-, m-, and p-xylenes, and ethylbenzene.

About 12 years ago, on the suggestion of S.S.Nametkin, at the Petroleum Chemistry Laboratory, Petroleum Institute, Academy of Sciences USSR, Pokrovskaya and associates commenced the synthesis and systematic study of the properties of naphthene-aromatic hydrocarbons, combined with cyclopentyl and cyclohexyl radicals (Bibl.138-148), and subsequently prepared a large number of individual compounds.

The synthesized hydrocarbons were characterized by their physical constants, and the purity of most of them was determined by the thermographic method developed by N.I.Lyashkevich at the Petroleum-Chemistry Laboratory.

The following hydrocarbons were synthesized:

1. Alkylaromatic;
2. Mono-, di- and trimethylbenzene with cyclohexyl and cyclopentyl rings attached to the aromatic nucleus;
3. Naphthalene and ethylnaphthalene with cyclohexyl and cyclopentyl rings as substituents;
4. Tetralin and diphenyl with a hexyl chain attached to the aromatic ring;
5. Hydrocarbons of the indane series with alkyl radicals in the aromatic nucleus, and indane with cyclohexyl rings in the aromatic nucleus;
6. 1,4-dicyclohexylcyclohexane, 1,3,5-tricyclohexylcyclohexane, 1,4-dimethylcyclopentylcyclohexane, 1,3,5-trimethylcyclopentylcyclohexane,

dicyclopentylcyclohexane, methylcyclopentylcyclohexane, cyclohexyl- and methylcyclohexyl decalin, cyclopentyl- and methylcyclopentyl decalin.

The near-ultraviolet absorption spectra of the above hydrocarbons were studied at the Laboratory of Petroleum Physics and Physical Chemistry, Petroleum Institute, Academy of Sciences USSR, using the photoelectric method (Gal'pern, Kusakov, Shimanko), and the photographic method (Kusakov, Shishkina). These included twelve cyclohexylbenzenes, ten cyclopentylbenzenes, four naphthalenes, and eleven indane derivatives (Bibl.149, 150). The study showed these compounds to possess rather characteristic near-ultraviolet absorption spectra. This made these spectra useful in establishing the positions of the substituents in the above compounds.

The absorption spectra in the near-ultraviolet were obtained for the first time for almost all the naphthene-aromatic hydrocarbons under study.

Up to now there have been almost no investigations on the effect of cycloalkyl substituents on the absorption spectrum of benzene in the near-ultraviolet.

It was found that the absorption spectrum in the near-ultraviolet is very similar in appearance for both cyclohexyl- and cyclopentylbenzenes.

It was found that, depending on the character of the substituent in the benzene ring (methyl, other alkyl, cyclopentyl, or cyclohexyl groups), there is a slight shift in the wavelength of the maxima of the absorption bands and a change in their relative intensity. These changes depend primarily on the nature, number, and mutual position of the substituents in the benzene ring. If the absorption spectra of these compounds are examined under the same instrument and under the same experimental conditions, the data may be used to identify individual compounds.

The absorption spectra of indane and its homologs were obtained by Shishkina with a spectrograph and were also recorded with the recording spectrophotometer at the Optical Laboratory of the INEOS, Academy of Sciences USSR, under the direction of I.V.Obreimov. These spectra are of considerable interest, in view of the very inaccurate existing data on certain of these compounds.

The accumulation of information about the absorption spectra of individual compounds will make it possible to use the method of near-ultraviolet absorption spectral analysis to investigate the structural and group composition of the kerosenes and, in some cases, also of the higher boiling petroleum fractions.

To elucidate the group features relative to the character of the mutual position, structure, and number of the naphthalene and aromatic rings and the influence of alkyl substituents on these features, Gal'pern, Kusakov, and Smirnov studied the infrared absorption spectra of nine individual naphthene-aromatic compounds: cyclohexylbenzene, cyclohexyl o-, m-, and p-xylenes, cyclohexylmesitylene and cyclopentyl o-, m-, and p-xylenes as well as cyclopentylmesitylene. Except for cyclohexylbenzene, this was the first time that the infrared spectra of these substances, synthesized at the Pokrovskaya Petroleum Chemistry Laboratory, were found (Bibl.149).

An analysis of these spectra showed that the absorption bands characterizing the type of substitution of the benzene ring in alkylbenzenes are, in the main, preserved in these compounds as well. Certain differences were also found in the spectra of cyclohexyl- and cyclopentyl- substituted benzenes of similar structure, giving reason to expect that it will be possible to determine the type of the naphthene constituent from the infrared absorption spectra.

Zimina, Ioganson, and Siryuk (VNII NP) (Bibl.151), using an IKS-11 spectrometer*, have worked out a method of quantitative determination of the CH_2-group content in mixtures of naphthene-paraffin hydrocarbons. A check of this method on artificial mixtures containing C_{12} saturated hydrocarbons showed its accuracy to be $\pm$ 1%. The same authors also investigated, from the infrared absorption spectra, the types of unsaturated structures of the monoolefins in thermally cracked kerosenes, and for a number of catalytic-cracked motor and aviation gasolines.

Shumulyakovskiy, Aleksandrov, Kurtsinovskaya, and Savost'yanova (Bibl.152) have

*The literature data were used to calibrate the instruments for individual substances.

described a rapid method of determining the total aromatic hydrocarbons in gasolines using the SF-4 spectrophotometer in the region of the harmonics of the C-H vibrations, based on the assumption that the ratio between the individual components (benzene, toluene, xylenes) varies only insignificantly.

The character of the ultraviolet absorption spectra from 2000 to 4000 Å permits them to be used mainly for the analysis of aromatic compounds: benzenes, naphthalenes, tetralins, indanes, diphenyls, and other more complex polycyclic compounds. In conjunction with the catalytic dehydrogenation method, the ultraviolet absorption spectra permit a study of the structure and composition of cyclohexane and decalin hydrocarbons, and of certain others.

When kerosene fractions contain a large number of isomers, and also as a result of the relatively low selectivity of the ultraviolet absorption spectra, it is impossible to investigate the individual composition of the C_9-C_{12} aromatic fractions.

The study of the ultraviolet absorption spectra is the most effective method, and sometimes even the only possible method, of qualitative analysis of naphthalenes and higher polycyclic aromatic hydrocarbons, which have characteristic and intense absorption bands in the long-wave region of the spectrum (3000 - 4000 Å). At the Petroleum Institute, Academy of Sciences USSR, A.V.Topchiyev, L.M.Rozenberg, Ye.S.Pokrovskaya, S.S.Nifontova, M.M.Kusakov, M.V.Shishkina, and others have commenced to work out a method for investigating the hydrocarbon composition of straight-run kerosenes. This study is being conducted as follows: The straight-run kerosene is distilled into wide cuts which are then separated chromatographically into naphthene-paraffin and aromatic components. The condensed aromatic hydrocarbons are studied by the picrate method, and by the near-ultraviolet absorption spectra. The fractions of mono- and bicylic aromatic hydrocarbons freed from the condensed aromatic hydrocarbons, are next distilled into more narrow cuts. The composition of the narrow cuts of aromatic hydrocarbons so separated is then investigated by the ultraviolet absorption spectral method. To separate the normal paraffins, the naphthene-

paraffin portion is treated with carbamide. The normal paraffins separated are then microfractionated.

The naphthene-isoparaffin portion of the cuts is subjected to an analytical dehydrogenation according to N.D.Zelinskiy. The catalyzate obtained is then chromatographed to separate the aromatic hydrocarbons liberated from the pentamethylene-isoparaffins. The aromatic hydrocarbons separated are freed from the condensed hydrocarbons and are then fractionated into narrow cuts and studied chemically and spectroscopically. The structural-group composition of the mono- and bicyclic aromatic hydrocarbons is determined from the ultraviolet absorption spectra; the bicyclic condensed hydrocarbons are also investigated by the picrate method.

The kerosene fractions of Surakhan, Tuymazy and Romashin crudes were studied. A number of aromatic and naphthenic hydrocarbons were also separated from the kerosene fractions and identified.

On the basis of the experimental data obtained at the Petroleum Institute Academy of Sciences USSR, and as a result of an analysis of the literature data on the absorption spectra of individual alkylnaphalenes, it was found that, for one and the same type of substitution in the aromatic ring, the absorption maxima vary in wavelength and relative intensity only slightly with the structure of the substituent saturated groups. This peculiarity of the ultraviolet absorption spectra was the basis for the structural-group analysis of the mono- and bicyclic aromatic ligroin-kerosene fractions with a boiling range of 160 - 300°C (Bibl.153 - 160).

Kusakov and Shishkina successfully applied the near-ultraviolet absorption spectra to the study of narrow cuts of monocyclic aromatic hydrocarbons separated from Romashkin and Tuymazy kerosenes before and after analytical dehydrogenation, and from Surakhan kerosenes after dehydrogenation (Bibl.149 - 160).

It was found that the maxima and the points of inflection in the absorption bands of various fractions (in the boiling range of 160-300°C) correspond to the characteristic absorption maxima of alkylbenzenes of certain substitution types.

A comparison of the absorption spectra of narrow monocyclic aromatic fractions with the absorption maxima in the near-ultraviolet that are characteristic for alkylbenzenes and, in individual cases, with the spectra of individual methylbenzenes, showed that Romashkin kerosene contains alkylbenzenes with a definite number and position of the substituent groups, as well as pseudocumene, durene, and isodurene.

In all, in the fractions of monocyclic aromatic hydrocarbons from Romashkin and Tuymazy kerosenes, the presence of monoalkylbenzenes, p- and m-dialkylbenzenes, tri- and tetraalkylbenzenes was established. Tetralin was detected in one of these fractions.

The spectra of the alkylbenzenes in Romashkin, Tuymazy, and Surakhan kerosenes showed the presence of alkylcyclohexanes with a definite number of substituent groups, in definite positions. The absorption spectra and, consequently, the structural-group composition of the hexamethylene hydrocarbons from the Devonian crudes of Romashkin and Tuymazy are very similar in the boiling range of 200 - 300°C.

The tetra-substituted benzenes are only weakly represented in the spectra of a number of aromatic fractions separated from dehydrogenated Surakhan kerosene, which indicate that the concentration of tetraalkylcyclohexanes is lower in the Surakhan kerosene than in the Tuymazy and Romashkin products.

A study of the structural-group composition of the monocyclic aromatic fractions on the basis of the ultraviolet absorption spectra is possible only when the naphthalene hydrocarbons are present in amounts not exceeding thousandths of a percent.

Ultraviolet spectroscopy may be recommended as a reliable method of checking the degree of separation of the monocyclic aromatic hydrocarbons from the condensed bicyclic hydrocarbons.

In examining the spectra of fractions consisting of bicylic condensed aromatic hydrocarbons, the presence of monocyclic hydrocarbons causes no trouble, and it is only rather large amounts of polycyclic condensed hydrocarbons (10 - 12%) that pre-

vent a spectral determination of the narrow-group composition of the naphthalenes.

From the absorption spectra of fractions of naphthalene hydrocarbons of Romashkin kerosene (200 - 300°C), a number of methylnaphthalenes and dimethylisopropylnaphthalenes were identified, together with 1,4,5,7- and 2,3,6,7-tetramethylnaphthalenes (Bibl.157).

Traces of naphthalene, and of its mono-, di-, and tri-substituted homologs, were detected by the ultraviolet absorption spectra, in the dehydrogenation product of Tuymazy kerosene, in concentrations impermissible for the picrate method (Bibl.155).

The methodological development of the Raman-spectrum method of investigating the hydrocarbon composition of the kerosene fractions of petroleum is now being continued at the Petroleum Institute, AN SSSR.

In addition to the work at the Petroleum Institute AN SSSR on the composition of kerosene fractions by means of the ultraviolet absorption spectra, Zimina and Suryuk (Bibl.136), at the VNII NP, have determined the total naphthalene hydrocarbons in the aromatic fractions of Romashkin and Tuymazy kerosenes. The content of individual hydrocarbons, naphthalene, 1- and 2-methylnaphthalenes was also determined from the absorption spectra in the low-boiling fractions of these kerosenes.

* * *

We have attempted in this sketch to give a short survey only of the principal work on the study of the composition of the light fractions of USSR crudes. We have paid particular attention to the work connected with the N.D.Zelinskiy school.

As will be clear from this survey, the work on the composition of the petroleum fractions, until the late 1930's, referred primarily to the group chemical characterization of the light gasoline and gasoline-ligroin fractions of petroleum. In the 1940's, methods of studying the individual composition were developed for the light fractions and were successfully applied to the examination of USSR crudes.

In connection with USSR development of the construction of aircraft and automobile engines and expansion of the chemical industry, the requirements for the quality of engine fuels and of raw materials for industrial organic synthesis were modified. It now became necessary to make detailed studies of the hydrocarbon composition of the benzene-kerosene fractions of petroleum.

On passing to the study of the ligroin-kerosene fractions, efforts were again directed toward developing methods of group analysis, but now on a higher basis, with further differentiation of the subgroups of hydrocarbons.

It is obvious today that the study of the structure and properties of the hydrocarbons contained in petroleum fractions and petroleum products is not only necessary for a rational selection of fuels for various engines, but also to reveal the resources of hydrocarbons, saturated and unsaturated alike, which are used in petrochemical synthesis.

On the other hand, it is also obvious that, to establish an experimentally based theory of the origin of petroleum and its changes under the conditions of migration, the field must not be confined to purely geological and geochemical factors. To solve the problem of the extraction of petroleum, it is essential considerably to deepen and broaden the experimental data on the nature, concentration, and structure of the hydrocarbon and non-hydrocarbon components, and of the organosulfur, nitrogenous, and oxygenous compounds entering into the composition of petroleum.

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